#### Poster Abstracts

Connecting Research and Practice: A Dialogue between ATSDR and the NIEHS Superfund Research Program

#### A Bioregional Approach to Community Engagement and Toxic Substances

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This presentation begins with the following hypothesis: A bioregional approach to knowledge integration, science communication, and environmental public health action is an effective way to prevent harmful exposures and diseases related to toxic substances. The UC San Diego Community Engagement and Research Translation Cores are collaborating with nonprofit organizations and business groups that are developing bioregional science, technology, and infrastructure. Bioregionalism provides an increasingly sophisticated and much needed conceptual, ethical, and practical guide to healthy and sustainable living. Critical bioregionalism advocates "rooted" community development where prospects for human health and wellbeing are understood as embedded in—and dependent upon—the local integrity and health of the community's land, watersheds, foodsheds and ecosystems. Bioregionalism becomes "critical" when it aims to eradicate root causes of poverty, social injustice, and environmental degradation while taking into account the world's increasingly globalized flows of material, energy, and knowledge resources.

Based on cases and lessons learned in the San Diego-Tijuana city-region over the past decade, this presentation will define strengths and weaknesses of the bioregional approach as it relates to the NIEHS Superfund Research Program (SRP) and ATSDR mission. Specifically, the talk will highlight two sets of lessons learned in the course of doing community engagement as part of UC San Diego's SRP.

- 1. Integrative bioregional concepts, including foodshed, watershed, socio-ecological systems, and land ethic have an increasingly vital role to play in framing environmental public health and how to prevent harmful exposures and diseases related to toxic substances. The alternative food movement taking place across the USA and worldwide (including support for urban agriculture and community gardens) is an especially fertile framework for community engagement given how it ties together concerns about cancer, soil/water contamination, obesity, health, and land use.
- 2. Building the capacity of civil society (community groups and social networks) to partner with universities and other research entities requires new equitable means for coproducing, sharing, and applying knowledge. But the enabling infrastructure and institutional support needed for this kind of knowledge-action collaboration is sorely lacking. Fortunately, a range of creative initiatives are emerging to close this gap, including: (a) new web systems that community-based organizations can use to clarify and share their priorities for use-inspired, problem-solving, and solutions-oriented research; (b) collaborative programs that incentivize citizens, scientists, entrepreneurs, and others to innovatively pool/share research-based evidence for public benefit; and (c) holistic "connect-the-dots" approaches to bioregional (urban-rural) sustainability and visualization that integrate otherwise fragmented efforts in the quest for justice, environmental health, and good jobs.

#### Resources

- On April 16, 2011, our SRP's Community Engagement Core co-hosted a <u>Food Justice Forum</u> that combined a scientific introduction with a follow on roundtable and open public dialogue.
- Global ARC Superfund Challenge: Environmental public health, the built environment and planning
- TV documentary that interconnects watershed management and environmental public health
- Pezzoli, Keith, Robert Tukey, Hiram Sarabia, Ilya Zaslavsky, Marie Lynn Miranda, William A. Suk, Abel Lin, and Mark Ellisman. 2007. The NIEHS Environmental Health Sciences Data Resource Portal: Placing Advanced Technologies in Service to Vulnerable Communities. Environmental Health Perspectives. 115 (4) 564-571. <a href="mailto:dx.doi.org/10.1289/ehp.9817">dx.doi.org/10.1289/ehp.9817</a>

#### A Functional Genomics Approach in Yeast: The Role of DNA repair in Trichloroethylene Toxicity

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Trichloroethylene (TCE) is a common drinking water and Superfund site contaminant implicated as a human carcinogen. Previous studies have shown the TCE metabolite, DCVC, as a renal toxicant, yet the molecular events mediating renal toxicity remain convoluted. Using a functional genomics approach in yeast, we aimed to gain a better understanding of TCE renal toxicity mechanisms. The yeast deletion library was treated with DCVC to identify genes required in response to exposure. Enrichment analysis of microarray results revealed an overrepresentation of genes involved in mutagenic DNA repair processes. Flow cytometry was used to confirm sensitivity of translesion synthesis (TLS) and nucleotide excision repair (NER) deficient strains. These pathways exhibited greater DCVC sensitivity in comparison to other DNA repair pathways. In particular, the lacking polymerase zeta and upstream NER genes were greatly affected. These two distinct pathways collaborate to repair DNA interstrand crosslink damage in yeast and higher organisms. These preliminary results suggest DCVC exposure results in similar DNA damage. NER mutants were more sensitive to DCVC exposure compared to TLS mutants, which further supports DNA interstrand crosslinks. The involvement of the error prone translesion synthesis repair can increase the rate of mutations and result in genome instability. Mutagenesis of important oncogenes can have implications for increased renal toxicity and cancer. In conclusion, preliminary data in yeast suggest an important role for DNA damage and repair mechanisms in mediating TCE renal toxicity.

### Arsenic Species Have Differential Impacts on *Pseudomonas aeruginosa* Induced Immune Response in Human Bronchial Epithelial Cells

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Arsenic is the number one environmental contaminant of concern with regard to human health. In animal and epidemiological studies, arsenic exposure has been associated with a variety of deleterious health outcomes, including increased cancer risk, cardiovascular disease, diabetes, and reproductive and developmental problems. Additionally, in utero and early life stage exposure to arsenic has been linked to lung disease, including acute and chronic bacterial infections, chronic obstructive pulmonary disease (COPD), and bronchiectasis, all of which are associated with Pseudomonas aeruginosa (Pa) infections. Animal models have also shown that chronic arsenic exposure decreases the immune response to viral challenge and that immune genes are down regulated in these animals. However, little is known about the mechanisms by which these alterations in immune response occur or the relative contributions of different arsenic species at low, environmentally relevant exposures observed in the U.S. Accordingly, this study examined the impacts of inorganic sodium arsenite (iAs<sup>III</sup>) and two major metabolites, monomethylarsonous acid (MMA<sup>III</sup>) and dimethylarsenic acid (DMA<sup>V</sup>), on Pa induced cytokine secretion by primary human bronchial epithelial cells (HBEC). ICP-MS studies revealed that HBEC do not metabolize any species of arsenic, making this a useful model to examine species-dependent effects. A panel of 42 cytokines was measured after stimulation with Pa in HBEC exposed to one of the three species of arsenic. HBEC from four different donors exposed to 10 ppb DMA for 6 days had significantly decreased IL-8, IL-6, Gro-a and Gro-b cytokine secretion after Pa stimulation than cells exposed to Pa alone. In contrast, exposure to 10ppb  $iAs^{III}$  did not alter Pa-induced cytokine secretion, whereas exposure to 10 ppb MMA<sup>III</sup> increased Pa-induced IL-8, and Gro-b secretion in HBEC. HBEC exposed to 10 ppb DMA<sup>V</sup> also exhibited significantly decreased mRNA levels of IL-8, IL-6, CXCL1 (Gro-a), and CXCL2 (Gro-b) after Pa stimulation in comparison to Pa alone. These data provide the first evidence of arsenic species-dependent alterations of the immune response of human bronchial epithelial cells to infection by Pa. IL-8, IL-6, Gro-a and Gro-b are key proinflammatory cytokines that recruit monocytes, macrophages, and neutrophils that clear Pa infections from the lungs. Thus, low, environmentally relevant levels of MMA<sup>III</sup> and DMA<sup>V</sup>-induced changes in cytokine secretion by human bronchial epithelial cells in response to Pa are likely to contribute to the increased incidence of acute and chronic bacterial infections, COPD, and bronchiectasis observed in individuals exposed to arsenic. Moreover, the data also suggest that the iAs<sup>III</sup> metabolites MMA<sup>III</sup> and DMA<sup>V</sup> have significant impacts on the innate immune response of human lung cells to Pa infection.

#### Association of Carcinogenic PAH Emissions with Lung Cancer Mortality Rates on a Global Scale

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Four out of five lung cancer cases have been linked to tobacco smoking. Other factors, including diabetes, obesity, and personal income, have been associated with lung cancer rates. Air pollution, containing carcinogenic polycyclic aromatic hydrocarbons (PAHs), may also contribute to lung cancer occurrence and mortality. However, a clearer understanding of the contribution of air pollution (and carcinogenic PAH exposure) to lung cancer occurrence and mortality is needed for better risk characterization, especially on a global scale.

The estimated number of lung cancer deaths per 100,000 people in 2004 and age standardized lung cancer death rate per 100,000 people in 2004 were regressed on smoking prevalence, cigarette price, GDP per capita, number of people with diabetes, average body mass index (BMI) and carcinogenic PAH emissions (in benzo[a]pyrene equivalence) using multiple linear regression and data from 136 different countries. The contribution of carcinogenic PAH emissions to lung cancer mortality rates was assessed for countries with different socioeconomic groupings.

A statistically significant positive correlation (p < 0.05) between the estimated number of lung cancer deaths per 100,000 people and benzo[a]pyrene equivalent emissions was found for the high income level group (countries with GDP per capita > \$10,065 USD) and not for low ( $\leq$  \$825 USD per capita), low middle (\$826 to \$3,255 USD per capita), and upper middle (\$3,256 to \$10,065 USD per capita) income level groups. For every 10% increase in the mean BaPeq emissions, a 0.80% increase in the median number of lung cancer deaths per 100,000 people was observed for the high income level group. Similarly, a 10% increase in smoking prevalence resulted in a 4.5% increase in the median number of lung cancer deaths per 100,000 people for the high income level group (p < 0.05). There was a statistically significant positive correlation (p < 0.05) between smoking prevalence and lung cancer mortality rates when all income level groups were combined. There was a statistically significant negative correlation (p < 0.05) between cigarette price and the age standardized lung cancer death rate per 100,000 people when all income level groups were combined.

This study is the first to link PAH emissions with lung cancer on a global scale. For the high income level countries, a 10% increase in mean BaPeq of PAH emission was associated with 0.80% increase in median number of lung cancer deaths. A 10% increase in smoking prevalence was associated with 8.79% and 4.90% increase in the median number of lung cancer deaths (*ED100000* and *ASDR100000*) in the world, respectively. Future assessment of lung cancer risks should take into account air pollution.

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- 5. World Health Organization (WHO) Mortality database, 2009

### Cohort Urine Exposome Library from Puerto Rico, an Island with Many Superfund Sites and a High Incidence of Preterm Birth

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The incidence of preterm birth has increased up to about 12% over the last 20 years in the United States. During the same period, it has climbed to about 19% in Puerto Rico, an island with many Superfund sites. Potentially, exposure of pregnant women to environmental contaminants contributes to preterm birth. We are establishing a cohort urine exposome library set up as a collection of urine extracts from pregnant women in Puerto Rico. This library is being formed by the following sequence of steps:

- 1. Throughout a week in her home during her first trimester, a pregnant woman fills a 0.5 gallon jar (containing a preservative) with first-void urines;
- 2. A nurse picks up the jar and conducts two solid phase extractions at a hospital with a stirring porous extraction paddle (PEP), comprising first a caged tea bag containing 2 grams of mixed, particulate adsorbents and then a second tea bag having 2 grams of Carboxen, a carbon adsorbent; and
- 3. The PEPs are sent to Northeastern University for processing, storage, and analysis.

This technique for extraction has some advantages, such as practical, nonclogging, use in the field, and use of equilibrium conditions for high reproducibility. From each stored extract, many aliquots can be taken for testing various classes of chemicals, for confirmatory testing of initial positive results (chemicals that are elevated in the preterm urines), and for use in future epidemiology studies. We will be testing aliquots from this library in a targeted/nontargeted way by mass spectrometry to potentially discover xenobiotics from Superfund sites that contribute to preterm birth. The work is sponsored by NIEHS Grant P42ES017198 that is awarded to PROTECT (Puerto Rico Testsite for Exploring Contamination Threats), a Superfund Research Program focusing on preterm birth and centered at Northeastern University.

### Development and Validation of Complementary LCMS and GCMS Methods to Examine Oxygenated-PAHs (OPAHs) in Environmental Analyses

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Despite the reports of oxygenated polycyclic aromatic hydrocarbons (OPAHs) in publications for over three decades, quantitative analyses of this class of compounds have only started to make significant advances within the last few years. OPAHs, alternatively labeled oxy-PAHs, have one or more oxygen attached to the aromatic ring structure and may also contain other chemical groups. OPAHs may be formed from petrogenic or pyrogenic sources but also through chemical oxidation, photo-oxidation, or biological transformation of un-substituted PAHs. Additionally, it has been observed that OPAHs are persistent in the environment, as opposed to other ephemeral intermediates of degradation processes, and there is evidence that some OPAH compounds are more toxic than the parent PAHs. Analysis of this wide ranging physiochemical class of compounds is challenging. OPAHs are more polar compared to their PAH analogues, which directly affects their range of solubilities in solvent systems. The wide range of solubility necessitates techniques to ensure solvation and stability, and ionization of a target compound of this class may or may not be optimal for just one ionization source or chromatography system. In previous studies, both gas chromatograph (GC) and liquid chromatograph (LC) mass spectroscopy (MS) methods have successfully quantitated OPAHs in environmental samples; however, by typically targeting fewer than 10 compounds, environmental investigations are limited. Using parallel and complementary methods of LC/APCI/MS and GC/EI/MS to analyze a suite of OPAH compounds has not been reported in any literature sources to our knowledge. In this study, the objectives were to optimize each method for increased accuracy and precision of an expanded target analyte list of OPAHs from previous reported methods, and to produce a complementary set of validated methods able to quantify 24 OPAH compounds (log Kow 0.2-4.81) in addition to labelled and deuterated standards. Combining methods provides for the identification and quantitation of all 24 OPAHs, with 19 compounds shared between methods and 3 quantitatively determined by GCMS (Xanthone, Chromone, and Perinapthone) and 2 by LCMS (1,6-Benzo[a]pyrenedione, and 7,8-Benzo[a]pyrenedione). Using 6 calibration standards on each instrument, all 22 OPAHs in the GCMS method were within 15% accuracy, and had less than 15% relative standard deviations (RSDs), while the LCMS quantitated 19 of 21 non-labelled compounds within 20% accuracy, and less than 15% for RSDs. Limits of detection ranged from 0.006-0.528 μg/mL using the GCMS and only 0.010-0.021 μg/mL on the LCMS. After method validation, both methods were used to examine OPAHs in complex mixtures from the Portland Harbor Superfund site in Oregon. Using passive samplers deployed at this site, several semi-polar organic compounds were identified in the complex extract mixture, including OPAHs. Current work will quantify any additional OPAHs present in the extracts using both complementary methods for a full analysis of 24 OPAH compounds.

#### **Estimation of Preferential Contaminant Transport in Karst Groundwater Systems**

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Karst groundwater systems are highly productive and provide an important freshwater resource for human development and ecological integrity. Their high productivity is often associated with conduit flow and high matrix permeability. The same characteristics that make these aguifers productive also make them highly vulnerable to contamination and a likely route for contaminant exposure. Of particular interest are chlorinated volatile organic contaminants and phthalates derived from industrial solvents and plastic byproducts. These chemicals have been identified as potential precursors of preterm birth, a leading cause of neonatal complications with a significant health and societal cost. The general objectives of this work are to: (1) develop fundamental knowledge and determine the processes controlling the release, mobility, persistence, and possible pathways of contaminants in karst groundwater systems and (2) characterize transport processes in conduit and diffusion-dominated flow under base flow and storm flow conditions. The work presented herein focuses on the development of geo-hydro statistical tools to characterize flow and transport processes under different flow regimes. Multidimensional, laboratory-scale Geo-Hydrobed models were developed and tested for this purpose. The models consist of stainless-steel tanks containing karstified limestone blocks collected from the karst aquifer formation of northern Puerto Rico and integrate a network of sampling wells to monitor flow, pressure, and solute concentrations temporally and spatially. Experimental work entailed making a series of point injections in wells while monitoring the hydraulic response in other wells. Statistical mixed models were applied to spatial probabilities of hydraulic response and weighted injected volume data and were used to determinate the best spatial correlation structure to represent paths of preferential flow in the limestone units under different groundwater flow regimes. Transport experiments were also conducted using a CaCl<sub>2</sub> tracer to validate the preferential-flow path estimates and characterize dual porosity transport. Testing of the karstified models show that the system can be used to represent the variable transport regime characterized by conduit and diffuse flow in the karst systems. Initial hydraulic characterization indicates a highly heterogeneous system resulting in large preferential flow components. The preferential flow network areas tend to increase with increasing groundwater flow, suggesting that there is a greater volume of the system being influenced by the contaminated water at higher flow rates. Temporal distributions of Cl in the model show varying response according to the location of the sampling cluster and support the preferential flow network distribution generated from the statistical modeling of the flow experimental data. Extended spatial distribution and high degree of tailing of Cl at later times indicate transport from zones of preferential flow to regions of lower permeabilities influenced by diffuse transport. The hydraulic statistical approach and the hydrodynamic information obtained from tracers are applied to assess fate and transport processes of CVOCs and phthalates as single components and mixtures in karst groundwater system. This work is supported by the National Institute of Environmental Health Sciences (NIEHS, Grant Award No. P42ES017198).

### **Evaluating the Effects of Bioremediation on Genotoxicity of PAH- Contaminated Soil Using Genetically Engineered, Higher Eukaryotic Cell Lines**

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Bioremediation is one of the commonly applied remediation strategies at sites contaminated with polycyclic aromatic hydrocarbons (PAHs). As of 2005, bioremediation had been used at 26% of the PAH-contaminated Superfund cleanup sites, more than any other single remediation technology. Bioremediation, as well as other remediation technologies, are typically evaluated based on the removal of target pollutants rather than on broader measures related to human health risks. For risk assessments of PAH-contaminated sites, US EPA guidelines generally only focus on un-substituted PAHs, most often the 16 priority PAHs. However, in most cases, it remains unknown whether the removal of the regulated 16 priority PAHs during bioremediation corresponds to a reduction in health risk. We investigated changes in the toxicity and genotoxicity of PAHcontaminated soil from a former manufactured-gas plant (MGP) site before and after two representative simulated bioremediation processes: simulated ex situ treatment in a laboratory sequencing batch reactor system and simulated in situ treatment in a long-term, continuous-flow column system. Toxicity and genotoxicity of the residues from solvent extracts of the soil were determined by DNA damage response analysis using the chicken DT40 B-lymphocyte isogenic cell line and its DNA-repair-deficient mutants. Although both bioremediation processes significantly removed PAHs from the contaminated soil (bioreactor 69% removal; column 84% removal), bioreactor treatment resulted in an increase in toxicity and genotoxicity over the course of a 7 d treatment cycle, whereas long-term column treatment resulted in a decrease in toxicity and genotoxicity. However, when screening with a battery of DT40 mutants for genotoxicity profiling, we found that column treatment induced DNA damage types that were not observed in untreated soil and that enhanced oxidative DNA damage was observed after the column treatment. Moreover, total organic residue instead of PAH concentration per se was significantly correlated with toxicity and genotoxicity of the soil. These results indicated that besides PAHs, other organic compounds were also responsible for the total toxicity and genotoxicity of the PAH-contaminated soil undergoing bioremediation. As a first step towards elucidating sources of genotoxicity, we have found significant concentrations of anthraquinone, phenanthrene quinone, fluorenone, and benzanthracene quinone in the contaminated soil, although preliminary results suggest that anthraquinone is removed during bioremediation. Overall, bioremediation is an effective tool to remove PAHs from contaminated soil, but different bioremediation strategies could lead to different outcomes of toxicity and genotoxicity for PAH-contaminated soil. Toxicity and genotoxicity bioassays can be an effective supplement to chemical analysis-based risk assessment for contaminated soil when evaluating the efficacy of bioremediation.

#### Expression of MTBE Degradation Genes in Methylibium petroleiphilum PM1

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MTBE is the primary organic groundwater contaminant in California, with low biodegradation rate under oxygen-limited conditions. Its downstream metabolite, tert-butyl alcohol (TBA), is a potential carcinogen increasingly encountered at sites historically known to be contaminated with MTBE. Since detection limits are low, oil companies are hard-pressed to clean up contaminated sites, and as of 2010, 7 years since the chemical was banned in the state, about 200 public supply wells in California have had to be taken offline. Methylibium petroleiphilum PM1 is a methylotrophic bacterium capable of completely degrading MTBE and TBA under aerobic conditions. The genes involved in degradation of these two compounds are mdpA (MTBE monooxygenase) and mdpJ/K (TBA hydroxylase). In this study, the expression levels of these genes were monitored by cDNA based RT-qPCR in microcosms containing resting cells of PM1 spiked with MTBE, TBA, pyruvic acid, and BTEX compounds. Both genes are significantly induced in the presence of MTBE and TBA over the course of 24-48 hours of exposure, whereas the expression levels in the presence of pyruvic acid stayed much lower and constant throughout the course of exposure. This provides conclusive evidence that the MTBE degradation pathway is induced in the presence of its substrates. In addition, expression levels of gene mdpC, encoding a putative transcriptional activator in the MTBE degradation gene-cluster, were also monitored and found to be low and constant during the course of exposure to MTBE. mdpC insertional mutant of PM1 has been created and is being analyzed for its role in the pathway. Furthermore, when PM1 microcosms were exposed to non-fatal dose of chloramphenicol, a prokaryotic protein synthesis inhibitor, in addition to MTBE, mdpA and mdpJ were expressed at much lower levels than in its absence, indicating that a protein intermediate may be involved in the induction of the pathway. With limited information available about this pathway at the genetic level in PM1, it is imperative to understand the regulation of the pathway to develop efficient approaches to improvise current bioremediation and monitoring strategies. This study will further drive our work on biosensor development for MTBE detection in environmental samples, which is currently being developed using a variant of the green fluorescent protein and promoter of gene mdpA.

#### Gene-Environment Interactions Suggest Race-Specific Genetic Determinants of Cadmium on Newborn Birth Weight

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Cadmium (Cd) is an established environmental toxicant that has been associated with various adverse health outcomes. In particular, Cd is a developmental toxicant and exposures during in utero periods can be a critical window of susceptibility. Prenatal exposures to Cd have been associated with unfavorable birth outcomes, including restricted growth parameters, such as low birth weight and decreased head circumference, as well as impaired neurobehavioral and physiological development in childhood. Racial disparities can exist with exposure to Cd and birth outcomes, yet the underlying genetic susceptibilities remain largely unknown. The interactions of genes and environmental contaminants during prenatal exposure to Cd warrant further investigation. In general, mechanisms of Gene  $\times$  environment (G  $\times$  E) interactions have been identified among susceptible populations exposed to environmental contaminants. Here, we examine the effects of Cd exposure and birth disparities, specifically focusing on maternal cadmium levels on newborn birth weight as well as the interactive effects of maternal genotype and cadmium exposure on birth weight. Multivariate analyses were used to assess the risk of low birth weight outcome resulting from maternal cadmium exposure alone as well as from an interactive effect with maternal genotype. We found that 1010 women (77.4%) had detectable levels of cadmium, with race-specific detection rates of 71.5% for NHW and 77.0% for NHB. Maternal cadmium levels and newborn birth weight were not significantly associated; however, infants born to NHB mothers had significantly lower birth weights. We identify relationships between four maternal genetic variants of inflammatory response genes among NHW women and newborn birth weight. However, our  $G \times E$  assessment revealed multiple racespecific and SNP-specific associations with newborn birth weight. Our study is the first to identify a  $G \times E$ association between genetic variants of cytokines and in utero cadmium exposure. Notably, we identify racespecific association between cytokines IL1A, IL2, IL4, IL12A, IL12B, and IL13 with newborn birth weight. Based on these results, early life exposures to cadmium may have detrimental effects on birth outcomes, including decreased birth weight.

### Improved Separation of Complex Polycyclic Aromatic Hydrocarbon Mixtures Using Novel Column Combinations in GC×GC/ToF-MS

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Complex mixtures of polycyclic aromatic hydrocarbons (PAHs) are difficult to resolve because of the high degree of overlap in compound vapor pressures, boiling points, and mass spectral fragmentation patterns. The objective of this research was to improve the separation of complex PAH mixtures (97 different PAHs, including parent, alkyl-, nitro-, oxy-, thio-, chloro-, bromo-, and high molecular weight PAHs) using GC×GC/ToF-MS by maximizing the orthogonality of different GC column combinations and improving the separation of PAHs from the sample matrix interferences and unresolved complex mixtures (UCM) usually present in complex environmental samples. Four different combinations of non-polar, polar, liquid crystal, and nano-stationary phase columns were tested. Each column combination was optimized and evaluated for orthogonality using a method based on conditional entropy that considers the quantitative peak distribution in the entire two-dimensional space. The highest chromatographic resolution, lowest synentropy, and highest orthogonality were achieved with column combination "C," consisting in a 10m × 0.15mm × 0.10µm LC-50 liquid crystal column in the first dimension and a 1.2m × 0.10mm × 0.10μm NSP-35 nano-stationary phase column in the second dimension. Environmental samples were then analyzed for complex mixtures of PAHs using column combination "C," including an atmospheric particulate matter with diameter < 2.5μm (PM<sub>2.5</sub>) sample from Beijing, China, a soil sample from St. Maries Creosote Superfund site, and a sediment sample from the Portland Harbor Superfund site. Column combination "C" resulted in low interference from UCM and thus better chromatographic separation and identification of PAHs. In addition, the use of this column combination in GC×GC/ToF-MS resulted in significantly shorter analysis times (176 min) for complex PAH mixtures compared to four different one-dimensional GCmethods that would be needed in order to complete the analysis of a complex PAH mixture containing parent, alkyl-, nitro-, oxy-, thio-, chloro-, bromo-, and high molecular weight PAHs using a one-dimensional GC/MS for a total run time of 257 min, as well as potentially reduced sample preparation time.

#### Heterogeneous Reactions of O<sub>3</sub>, OH radicals and N<sub>2</sub>O<sub>5</sub> with and with Chinese Particulate Matter to Simulate Trans-Pacific Atmospheric Transport

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In the atmosphere, polycyclic aromatic hydrocarbons (PAHs) partition between the gas and particulate phases depending on their chemical and physical properties and ambient temperature. In general, the PAHs with more than four aromatic rings are found primarily in the particulate phase, allowing them to undergo long range atmospheric transport. The reactivity of particulate-bound PAHs is considered to vary, to some extent, with the composition of particle (1). Previous heterogeneous reaction studies on particulate matter (PM) have used graphite, diesel soot, wood smoke and in-house soot samples (2-4). However, in this study, PM from Beijing, China, with an aerodynamic diameter  $< 10 \mu m$ , was exposed to  $O_3$ , OH radicals, and  $N_2O_5$  to simulate heterogeneous reactions that may occur during trans-Pacific transport. The PM samples were collected on prebaked quartz fiber filters over 24 h periods at an urban site in Beijing, China. The filters were cut into two portions. The first portion was quantitatively analyzed for PAHs, nitrated-PAHs (NPAHs) and oxygenated-PAHs (OPAHs); and represented the unreacted masses. The second portion was placed in a ~7000-L indoor all-Teflon chamber and exposed to either O3, OH radicals, or N<sub>2</sub>O<sub>5</sub>. The concentrations of O<sub>3</sub>, OH radicals, and N<sub>2</sub>O<sub>5</sub> used in chamber experiments, combined with the duration of the exposures, simulated trans-Pacific atmospheric transport of the PM (5). The quantitative analysis of both the unreacted and reacted portions of the filter was done using gas chromatography coupled with mass spectrometry, with using electron ionization for PAHs and negative chemical ionization mode for NPAHs and OPAHs.

The reaction of PAHs on PM with  $O_3$  resulted in a 16% - 48% loss in parent PAH concentrations. As expected, no significant NPAH products were observed in the  $O_3$  reaction.

For the OH-radical exposure, the parent PAH masses on PM decreased by 1% to 42%. Only 1-nitropyrene and 6-nitrobenzo[a]pyrene concentrations were found to increase significantly, while 9-nitroanthracene and 7-nitrobenzo[a]anthracene masses were found to decrease significantly upon exposure.

The  $N_2O_5$  was the most effective oxidant in transforming the particulate-bound PAHs, reducing the masses by 5% to 57%. Of the parent PAHs, benzo[a]pyrene showed had the largest percent decrease in concentration on the PM. The NPAH concentrations, including concentrations of 1-nitropyrene, 1-nitrotriphenylene, 6-nitrochrysene, 2-nitrotriphenylene and 6-nitrobenzo[a]pyrene, increased significantly, howeverwhile the concentration of, only 9-nitroanthracene decreased significantly. In contrast, there was no observation of 2-nitropyrene and 2-nitofluoranthene formations. This suggests the occurrence of heterogeneous reaction of PAHs with gas phase  $N_2O_5$ .

The reaction of PAHs on PM with O3 resulted in a 16% - 48% loss in parent PAH concentrations. However, due to large standard deviations, these decreases were not statistically significant. As expected, no significant NPAH products were observed in the O₃ reaction.

For the OH-radical exposure, the parent PAH masses on PM did not decrease dramatically and ranged from 1% to 42%. Only 1-Nitropyrene and 6-nitrobenzo[a]pyrene concentrations were found to increase significantly, while 9-nitroanthracene and 7-nitrobenzo[a]anthracene masses were found to decrease significantly after exposure.

For all three exposures, there was no observed increase in the concentrations of 2-nitropyrene and 2-nitrofluoranthene, two nitro-PAHs formed via gas-phase radical-initiated reactions, suggesting that the increase in other nitro-PAHs was due to the occurrence of heterogeneous reactions of PAHs with gas-phase species. Overall, these exposures simulating trans-Pacific transport did not significantly change the NPAH profile.

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# Improving Mechanistic Basis for Health Assessment of Trichloroethylene via Development of Analytical Methods for Quantification of S-(1,2-dichlorovinyl)glutathione and S-(1,2-dichlorovinyl)-L-cysteine in Blood, Liver and Kidney Samples

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Trichloroethylene (TCE) is a well-known environmental and occupational toxicant contaminating air, water, and soil. Since the beginning of its widespread production in the 1920s, an immense amount of data regarding TCE toxicity has been accumulated; however, there are still a number of unresolved issues and controversies regarding the mechanisms of TCE toxicity. The US EPA recently issued the final IRIS assessment of TCE and classified TCE as carcinogenic to humans. Still, several critical issues remain unresolved, such as the uncertainty in the amount of glutathione (GSH) conjugation metabolites formed in various tissues. US EPA postulated that TCE metabolites from the GSH conjugation pathway play a key role in the mechanism of kidney carcinogenesis. In the present study, we quantified S-(1,2-dichlorovinyl)glutathione (DCVG) and S-(1,2-dichlorovinyl)-L-cysteine (DCVC) in liver, serum, and kidney tissues collected from male mice from several inbred mouse strains (129S1/SvImJ, A/J, BTBR T+tf/J, C57BL/6J, CAST/EiJ, NOD/ShiLtJ, NZW/LacJ) that represent an inter-strain range of quantitative differences in TCE metabolism. TCE (600 mg/kg/day, in 5% Alkamuls EL-620 in saline, i.g.) was administered once daily for 1, 2, or 4 weeks. Liver, kidney, and blood were collected at 2 and 8 hrs after the last dose. DCVG and DCVC extraction procedures were optimized for each tissue. Both of the analytes were measured simultaneously by a heat-assisted electrospray ionization tandem mass spectrometry in positive ion mode. Serum, liver, and kidney levels of DCVC and DCVG varied considerably. This study confirmed that DCVC is detected in the kidney of mice exposed to TCE and provides new important quantitative data for cross-tissue and -strain comparisons of TCE metabolism via GSH conjugation.

#### Maternal Exposure to EPFR-Containing PM Predisposes to Enhanced Allergic Asthma in Offspring

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Environmentally persistent free radicals (EPFRs), with half-lives on the order of weeks, have been detected in association with airborne particulate matter (PM), and early exposure to environmental hazards, such as PM, has been associated with an increased incidence of asthma in childhood. We hypothesized that *in utero* exposure to EPFR-containing PM disrupts immune development resulting in aberrant immune responses and enhancing susceptibility to asthma. To test this hypothesis, we exposed pregnant mice to ultrafine particles containing persistent free radicals (EPFR-UFP) and determined postnatal immune development and response to allergen sensitization and challenge. Intrauterine exposure to EPFR-UFP inhibited pulmonary T helper (Th1/Th2/Th17) and T regulatory (Treg) responses in early life (<1 week of age). Th2 and Treg responses recovered to normal levels; whereas Th1 responses remained attenuated at 6 weeks of age. In the asthma model, intrauterine EPFR-UFP-exposed mice exhibited higher airway hyperresponsiveness and pulmonary eosinophilia. In addition, levels of IL-4 and IL-5 (Th2 cytokines) in the bronchoalveolar lavage fluid of these mice were significantly higher than that of non-exposed mice that were sensitized and challenged with ovalbumin. Our data suggest that *in utero* exposure to EPFR-UFP enhances adult asthma development in mice, which might be related to the inhibition of pulmonary Th1 maturation.

#### Measurement of Hydroxy and Parent-PAHs in Urine and Atmospheric Particulate Matter

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Humans are exposed to Polycyclic Aromatic Hydrocarbons (PAHs) through polluted air and diet. Broiled, smoked, or grilled food contain higher amounts of PAHs compared to uncooked or boiled food. In air, PAHs are emitted from incomplete combustion of fuels and are adsorbed on fine particulate matter, which can be deposited in lungs, causing adverse health effects and cancer. When in the human body, parent-PAHs are metabolized to hydroxy-PAHs and excreted via urine. Hydroxy-PAH composition of particulate matter (PM) and the hydroxy-PAH composition of urine, the metabolic pathways of PAHs can be studied.

An analytical method was developed to simultaneously measure 33 hydroxy-PAHs and 19 parent PAHs in urine and particulate matter using gas chromatography/mass spectrometry (GC/MS). Urine samples were deglucuronized with β-glucuronidaze/aryl sulfoctase and solid phase extracted (SPE) with the combination of C18 and Plexa stationary phases. PM was extracted from filters with the use of Accelerated Solvent Extraction (ASE). The urine extracts and aliquots of PM extracts were mixed with an internal standard and derivitized with *N*-methyl-*N*-tert-buthyldimethylsilyl-trifluoroacetamide (MTBSTFA). The derivatized samples were analyzed in electron impact ionization mode with GC/MS. Stable isotope labeled surrogates were used to account for loss throughout the analytical method.

Recovery experiments were conducted using a combination of C18 and Plexa SPE columns and elution with a 1:1 mixture of dichloromethane:ethylacetate. Most of the recoveries from urine ranged from 80 to 120%. PM recovery showed that dichloromethane should be used to extract the analytes when using ASE. Intra- and interday variability of the measurements and stability of the derivatized product were also investigated. Results showed that the 33 OH-PAH formed stable products over a two-week storage period. The stability of OH-PAHs in frozen urine was also studied. Results showed that many OH-PAH were stable in frozen urine for a one-week period. However, the dihydroxynaphthalenes were not stable in frozen urine for a one-week period.

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### Modeling Groundwater Flow and Contaminant Fate and Transport in the North Coast Karst Aquifer of Puerto Rico

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The goal of the PROTECT NIEHS SRP Center is to evaluate exposure to groundwater contamination through karst formations in Northern Puerto Rico and to assess the potential impact of said exposure on public health. This will be achieved through integrated analytical, mechanistic, epidemiology, and fate-transport studies, along with a centralized, indexed data repository. The fate and transport studies include coupling models for contaminant fate and transport in karst aquifers with Geographic Information System (GIS) mapping of historical detection data. A review of the fate and transport studies' approach and progress to date are presented.

Prediction of contaminant fate and transport in karst hydrogeological systems is complex due to the presence of a high degree of heterogeneity. Slow seepage through the rock matrix and fast flow through fractures and conduits result in a high temporal and spatial variation in aquifer behavior. Contaminant storage occurs in the rock matrix, but contaminant transport occurs mostly along preferential pathways in the conduit network. Computer models predicting contaminant fate and transport should account for combined matrix and conduit flow. The properties and location of the conduit network, however, are difficult to determine. This is further complicated by the presence of contaminants in NAPL (Non-Aqueous Phase Liquid) phase. While pooled NAPLs remain stationary under base flow conditions, NAPL pools can be dragged downstream or flushed in suspension during storm flows.

As part of this work, two models are being developed. A groundwater flow and contaminant fate and transport model is being developed to improve understanding. A distributed groundwater flow and transport model is being developed that includes the central part of the North Coast Limestone Aquifer of Puerto Rico. Because this large regional scale model utilizes data that are limited in some regions or have some degrees of uncertainty, a stochastic approach may be adopted to incorporate uncertainty assessments into the parameters and database used in the simulations. The model uses hydraulic parameters with probability distributions calculated from statistical data and results in outputs such as contamination plume, groundwater level, and flow rate with different probability distributions. The models will be developed at a smaller scale for transport of trichloroethylene (TCE) in the Vega Alta region, where extensive monitoring data and recent monthly weather data are available.

These models will be coupled with the use of Geographic Information Systems (GIS) techniques to improve development of monitoring schemes, predicting contaminant fate and transport, evaluating exposure pathways, and assessing health risks. The general approach involves collection, analysis, indexing, and segregation of

historical and newly-collected data obtained; development of time-dependent flow and distribution fields; and assessment of potential sources and contaminant routes. The data repository covers (i) historical data from more than 1000 wells, springs, and contaminated sites; (ii) data from biannual field sampling and analysis of 16 wells, 3 springs, and 120 tap water samples; (iii) continuous meteorological, surface water, and groundwater data; and (iv) biomedical data (i.e., urine, blood, pregnancy tissues).

#### Pathway-Based Prediction of Tumor Outcome for Environmental PAH Mixtures

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The polycylic aromatic hydrocarbons (PAHs) benzo  $[\alpha]$  pyrene (BAP) and dibenzo [def,p] chrysene (DBC) produce tumors in mouse skin, lung, liver, and breast and were recently elevated to Class 1 known and Class 2A probable human carcinogens, respectively. However, most human PAH exposures result from chemical mixtures of multiple PAHs. Currently, little is known about the relative potency, carcinogenic potential, and mechanisms of tumorigenesis for PAH mixtures. In this study, we utilized a pathway-based approach to classify PAH and PAH mixture exposures based on their carcinogenic potential in skin. Gene expression profiles were measured in skin of FVB/N mice collected 12 hours after initiation with BAP, DBC, or 1 of 3 PAH mixtures (diesel exhaust, coal tar, and cigarette smoke condensate). Overall, 922 probes were significantly (p<0.05) regulated compared to control across the study. Transcriptional signatures were determined for each PAH treatment and compared to tumor outcome to identify the molecular changes responsible for the earliest events of carcinogenesis. PAH exposure following a two-stage initiation/promotion skin tumor protocol resulted in tumor incidence and multiplicity profiles of DBC>>BAP=Mix2=Mix3>Mix1=Control, based on statistical significance. A Bayesian integration model was utilized to identify biological pathways predictive of PAH and PAH-mixture carcinogenic potential during initiation. Integration of probability matrices from four enriched pathways (p<0.05) resulted in 100% classification accuracy with leave-one-out cross validation, including pathways for DNA damage, apoptosis, response to chemical stimulus, and interferon gamma signaling. Network and transcription factor analysis of the predictive gene clusters further resulted in identification of the upstream transcriptional regulators associated with skin cancer. Overall, we observed distinct gene expression profiles linked to tumor outcome for PAHs and PAH mixtures. DBC treatment, which had the greatest tumor response, uniquely altered genes associated with cell cycle and DNA damage pathways mediated by p53 and c-Myc, while BAP and PAH mixtures containing coal tar were less carcinogenic and altered genes associated with metabolic and stress response pathways mediated by Arnt, Nrf2, and Sp1. This pathway-driven approach was successfully utilized to distinguish early regulatory events during initiation linked to tumor outcome and shows the potential of using short-term initiation studies for prediction of carcinogenesis by environmental PAH mixtures. These data further provide a "source-tooutcome" model that could be used to predict PAH interactions during tumorigenesis and provide mode-ofaction based risk assessment of environmental PAH mixtures. Supported by P42 ES016465, P42 ES016465-S.

### Quantification of Polycyclic Aromatic Hydrocarbon Mixtures in Standard Reference Materials Using in GC×GC/ToF-MS

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous compounds in the environment and originate from incomplete combustion of organic matter during energy and industrial processes. PAH derivatives can also be formed as byproducts of transformation reactions in the environment. Identifying and quantifying PAHs in environmental samples is of concern due to the carcinogenic and mutagenic properties of some isomers. Some PAHs derivatives, such as 1-Nitropyrene, have higher mutagenic and carcinogenic potential than its parent PAH. Other PAH derivatives, such as halogenated, are being studied due to their potential persistence, bioaccumulation, and toxic effects. The objective of this research was to develop a single analytical method to identify and quantify complex mixtures of PAHs, including alkyl-, nitro-, oxy-, thio-, chloro- and bromo-PAHs present in two standard reference materials (NIST-SRM1975: diesel extract, NIST-SRM1650b: Diesel particulate matter) in a single chromatographic analysis. A method based on comprehensive two-dimensional gas chromatography/time of flight mass spectrometry (GC×GC/ToF-MS) was developed and used. Two column combinations were tested, combination "A": 30m Rxi-5ms column in the first dimension followed by a 1.2m Rtx-17 column in the second dimension; combination "B": 10m LC-50 liquid crystal column in the first dimension followed by a 1.2m NSP-35 nano-stationary phase in the second dimension. Combination "B" showed greater orthogonality and separation from interferences and unresolved complex mixture (UCM) in a previous study. Five-point calibration curves were developed for a standard mixture of a total of 93 different PAHs, with an average R<sup>2</sup> of 0.994 in both column combinations. The quantitation was performed using the three highest modulated peaks for each compound and the ratio of internal standard to target in order to decrease the amount of error associated with quantitation processes in two-dimensional GC methods. For both column combinations, the results obtained corresponded well to the certified values for both standard reference materials within a 95% confidence interval, showing that combination "B" can provide good chromatographic separation and reliable quantification of complex mixtures of PAHs in environmental samples.

## The Influence of Low Temperature Thermal Treatment on Pentachlorophenol Contaminated Soils with Pentachlorophenol and Environmentally Persistent Free Radicals

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The effect of low temperature thermal treatment on soils from a former Superfund wood-treating site contaminated with pentachlorophenol (PCP) and the environmentally persistent free radical (EPFR), pentachlorophenoxyl, was determined. Two types of thermal treatment were employed: a closed heating (oxygen-starved condition) where the soil was heated under vacuum and an open heating system (oxygen-rich conditions), where the soil was heated in ambient air. The pentachlorophenoxyl EPFRs' and the PCP molecules' chemical behavior were simultaneously monitored at temperatures ranging from 25 °C to 300 °C via electron paramagnetic resonance (EPR) spectroscopy and GC-MS analysis, respectively.

EPR analyses for the closed heating treatment indicated EPFR concentrations were between 2-12 x  $10^{18}$  spins/g of soil, with a g-factor and linewidth ( $\Delta$ Hp-p) range from 2.00311 – 2.00323 and 4.190 – 5.472 Gauss, respectively. EPR monitoring of the open heating soils revealed slightly broader and weaker radical signals, with spin concentrations ranging from 1-10 x  $10^{18}$  spins/g of soil, g-factor ranging from 2.00327 – 2.00341, and ranging from  $\Delta$ Hp-p of 5.209 – 6.721 Gauss. These results suggest that the open heating resulted in the formation of a more oxygen-centered structure of the pentachlorophenoxyl radical or new similar radicals. The EPFR concentration reached a maximum of  $10 \times 10^{18}$  spins/g of soil at 100 °C for open heating and  $12 \times 10^{18}$  spins/g at 75 °C for closed heating. The EPFRs half-lives were found to be between 2 – 24 days at room temperature in ambient air. These results suggest low temperature treatment of soils contaminated with PCP can convert the PCP to potentially more toxic pentachlorophenoxyl EPFRs, which may persist in the environment long enough for human exposure.

# Three Different Demonstration Applications of an Innovative Air Sampling Technology to Address Community-based Environmental Exposures: Oil Spills, Legacy and Emerging Chemicals at Community-Industry Land Boundaries, and Introduction of Contaminants during Food Preparation

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Although communities often want and need chemical monitoring data to characterize chemicals in their environment or from their activities, air monitoring equipment is often cost prohibitive or technically impractical. We are further developing air monitoring bio-analytical tools that employ our passive sampling device (PSD). PSDs require no external power, require minimal training for quality controlled sampling, and can be quickly and inexpensively deployed. PSDs are capable of providing qualitative and quantitative characterization of exposure to the bioavailable vapor phase fraction of legacy and emerging contaminants in the atmosphere. We demonstrate our PSD's utility in three vastly different scenarios: before, during, and after the Gulf of Mexico Deepwater Horizon oil spill in spring of 2010, at the interface of community tribal lands and high intensity industrial activities, and finally in Native American fish smoking activities. Legacy and emerging PAHs were characterized for all three scenarios; analysis of PSD extracts using a 1,200 analyte screening method was also undertaken.

Acute chemical spills generally require a quick response, and often there is a significant or unknown exposure prior to elaborate air monitoring equipment setup. We deployed air PSDs prior to, during, and after shoreline oiling from the Gulf of Mexico Deepwater Horizon oil spill of 2010 in Louisiana, Mississippi, Alabama, and Florida. Emerging and legacy polycyclic aromatic hydrocarbons (PAHs) were quantified in the air PSD. PSDs were also screened for an additional 1,200 contaminants of concern. We demonstrate the utility of the air PSD to respond to acute chemical spills and to gather chemical data sets on a wide range of contaminants.

Communities adjacent to highly industrialized lands often want to understand the contribution of contaminants of concern from industrial activities to their ambient activities. The Swinomish Indian Tribal Community (SITC) offered their lands to further test our developing air PSD technology and to address these kinds of questions. PSDs were deployed at SITC, which borders a petroleum facility, continuously for a yearlong study; from these PSD samples, legacy and emerging PAHs were identified and quantified. The results indicate spatial and temporal trends that were related to the activities of the tribal community and the petroleum facility.

While PSDs have been demonstrated as a surrogate for fish for aquatic environment assessment, atmospheric PSDs have not been previously used as a surrogate for food for preparation technique assessment. Community-based requests often include understanding the effects of special food preparations that are culturally important. The Confederated Tribes of the Umatilla Indian Reservation (CTUIR) requested an assessment of their fish smoking methods. As part of a larger study, we deployed air PSDs during the CTUIR smoking events to further evaluate the utility of using our PSD as a surrogate for smoke-processed fish. In a side-by-side study, the

PSDs were paired with salmon during smoking. PAHs were quantified from the air PSD and compared with the smoked salmon. The results show excellent promise for an alternative method for assessing food smoking preparation techniques. Throughout these three studies, the OSU SRP Research Translation and Community Engagement Cores partnered to develop culturally appropriate messages and data interpretation including workshops, print materials, brochures, and Web-based information.

#### Using Yeast Functional Toxicogenomics to Decipher the Toxicity of Organochlorinated Pesticides

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Exposure to organochlorinated pesticides (OCPs) has been linked to neurotoxicity, endocrine disruption, and cancer, but the cellular mechanisms of toxicity remain largely unknown. It was hypothesized that a chemical genomics approach using a *Saccharomyces cerevisiae* gene deletion library could help elucidate the cellular mechanisms by which various OCPs induce toxicity. Pools of deletion strains were exposed in triplicate for five and fifteen generations to the IC20, 50% IC20, and 25% IC20 OCP concentrations. The oligo sequences unique to each deletion strain were PCR-amplified and hybridized to TAG4 arrays to identify sensitive, unaffected, and resistant strains. The overrepresented biological terms within the data assisted in the selection of individual deletion strains for growth curve experiments. It is demonstrated here that genes involved in transcriptional elongation, nitrogen utilization, and amino acid sensing are necessary for resistance to the toxaphene OCP. Analyses for the dieldrin OCP indicate that amino acid sensing and components of the pyruvate dehydrogenase complex are critical for cell survival under dieldrin exposure and that leucine rescues its toxicity. Future investigations will refine the mechanism(s) in yeast and perhaps examine how the knockout or knockdown of orthologs in higher organisms, such as *C. elegans* or human cell lines, affects OCP toxicity.